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Moving Beyond Mass-based Parameters for Conductivity Analysis of Sulfonated Polymers

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Acronyms list

6F: Hexafluoro bisphenol A based sulfonated poly(arylene ether sulfone)

BPSH: Biphenyl based sulfonated poly(arylene ether sulfone) H⁺ form

ESF-BP: Biphenyl based cross-linked sulfonated poly(arylene ether)

MVC: molar volume per charge (cm³ per ionomer/mole equivalent of acid group)

NAC: Number of atom per charge

IEC: Ion exchange capacity (mequiv/g)

PCV: percent conducting volume

PEM: Polymer electrolyte membrane

PFSA: Perfluoro sulfonic acid

λ : Hydration number

Abstract Proton conductivity of polymer electrolytes is critical for fuel cells and has therefore been studied in significant detail. The conductivity of sulfonated polymers has been linked to material characteristics in order to elucidate trends. Mass based measurements based on water uptake and ion exchange capacity are two of the most common material characteristics used to make comparisons between polymer electrolytes, but have significant limitations when correlated to proton conductivity. These limitations arise in part because different polymers can have significantly different densities and conduction happens over length scales more appropriately represented by volume measurements rather than mass. Herein, we establish and review volume related parameters that can be used to compare proton conductivity of different polymer electrolytes. Morphological effects on proton conductivity are also considered. Finally, the impact of these phenomena on designing next generation sulfonated polymers for polymer electrolyte membrane fuel cells is discussed.

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INTRODUCTION

Numerous sulfonated polymers have been developed for potential application in polymer electrolyte membrane (PEM) fuel cells. We chose to group the most highly studied polymers into three categories (i) poly(perfluorosulfonic acid)s (PFSA)s, (ii) styrene sulfonic acids (SSAs), and (iii) sulfonated aromatic or heterocyclic polymers (1, 2). Representative chemical structures of sulfonated polymers are shown in Scheme 1.

PFSA)s are copolymers of tetrafluoroethylene and perfluorovinyl ether with a pendant sulfonic acid group. PFSA)s include Nafion, which is considered the benchmark of sulfonated polymers for fuel cells (3). Alternative PFSA)s such as Flemion, Aciplex, Dow, Hyflon, and 3M, share similar chemistry, usually with minor modifications to the ionomeric side chains (4).

Styrene sulfonic acids are sulfonated polymers that replace the tetrafluoroethylene based backbones of PFSA)s with styrene. Styrene sulfonic acids includes BAM from Ballard, Dais Analytic's sulfonated styrene-ethylene-butylene-styrene (SEBS) polymers, and radiation-induced polystyrene graft polymers (5).

Sulfonated aromatic or heterocyclic polymers are based on high performance engineering thermoplastics. Sulfonated polyaromatics include sulfonated poly(arylene ether)s, sulfonated polysulfones, sulfonated poly(ether ether ketone)s, and sulfonated polynitriles (6-8). Sulfonated heterocyclic polymers contain polyimide, polybenimidazole, or other heterocyclic repeat units (9).

[Scheme 1]

The primary purpose of these electrolytes in fuel cell applications is to transport protons allowing half reactions to occur. It is for this reason that they tend to contain high concentrations of strong acids (typically, sulfonic acid groups). While proton conduction is the most highly studied property of these materials, they must also possess other properties such as electronic insulation, impermeability to reactants, and chemical and mechanical robustness. While most sulfonated polymers are excellent electron insulators and have reasonably low reactant permeability, increasing proton conductivity of mechanically stable sulfonated polymers remains a technical challenge. Current commercially available polymer electrolyte membranes typically exhibit proton conductivity of about 100 mS/cm under fully hydrated conditions, a level of conduction suitable for most applications. There has been a drive to increase conduction at low relative humidity due to implications of cost and efficiency for high temperature, low relative humidity performance in automotive applications.

Efforts to elucidate structure-composition-property relationships of polymer electrolytes have aimed at correlating specific metrics (physical or compositional properties of PEMs) to observed performance (for example, proton conductivity as a function of temperature and relative humidity). Here, we attempt to review the data in the literature specific to proton conductivity in terms of specific metrics, factors such as water uptake; ion exchange capacity (based on volume and mass); hydration number; and percent

conducting volume (a novel parameter, described in detail later). Limitations and advantages of each of these specific metrics are discussed. In particular, each of these metrics has limitations as they fail to consider aspects of structure and morphology. In order to address these issues we present a discussion on phase contrast and phase continuity to help provide a more complete picture of critical factors in the design of next generation PEMs.

Mass based water uptake and ion exchange capacity (IEC) are two commonly used metrics for studying proton conductivity trends. Water uptake is typically obtained from two simple measurements, the wet and dry weight of membranes. It is therefore one of the easiest metrics to obtain, and is calculated by:

$$WU \text{ (wt.\%)} = \frac{W_{(WET)} - W_{(DRY)}}{W_{(DRY)}} \times 100 \quad (1)$$

where, $W_{(WET)}$ and $W_{(DRY)}$ are polymer weight in wet and dry states.

Ion exchange capacity (IEC) is usually obtained from chemical structure (through simple calculation of atomic weight per acid group) and is sometimes verified by measuring acid content by titration. IEC is typically expressed by the moles of sulfonic acid per gram of dry membrane expressed in the units of milliequivalents per gram. Alternatively, equivalent weight (EW), the number of grams of dry membrane per mole of sulfonic acid groups is also commonly used (IEC and EW are inversely related).

Figures 1a and b plot proton conductivity versus water uptake and IEC, respectively, for a large cross-section of sulfonated polymer electrolytes (taken from 32 independent references in the literature, this same data is reproduced in several other Figures for different metrics) (10-41). These plots show a general trend that conductivity increases as water uptake and IEC increase. These are commonly reported trends and make sense because as polymers contain more acid groups it is reasonable to assume that water uptake and conductivity should increase. The trend exhibited is much clearer for water uptake versus conductivity than for IEC, but even for water uptake there is meaningful scatter in the data. At a given water uptake, conductivity values can vary by up to an order of magnitude. The data scatter involved with IEC is much larger, although trends within specific polymer families are often much clearer than the combination of data presented here. Perhaps, due in part, to factors illustrated in these plots, water uptake has been more commonly correlated with physical properties across polymer families while IEC is more often limited to use in comparisons of varying sulfonation level in the same family of sulfonated polymers (42, 43).

[Fig.1]

Both water uptake and IEC (as presented in Figure 1) are mass based parameters which introduce limitations. One obvious reason for the large data scattering in Figure 1 is that polymer systems can have significantly different densities, and the mass of the polymer is less relevant for proton conduction which happens over length scales that are more

appropriately represented by volume based metrics rather than mass. Volume based parameters have been introduced by several scientists (including us) although they still are not commonly reported in relevant studies. The reason for this largely stems from the ease of making mass based measurements or estimations. While volume based measurements are not particularly difficult they do require more effort, and for most studies in the literature (focusing on a single family of polymers rather than across widely different families of polymers), mass based trends still allow for insight to be gained. It is only when polymers are compared across families or under “non-standard” conditions (such as extremely high water uptake) that mass based measurements become significantly limited. In compiling the data put forth in this review, one area of concern is that density data for many of the polymers presented in the literature does not exist, and therefore the mass based measurements cannot easily be converted to volume related parameters. In this review, we present and summarize various volume related parameters for sulfonated polymers and correlate these parameters with proton conductivity. These parameters although in many ways more appropriate for comparison purposes compared to more commonly reported mass based parameters are still limited as they do not consider morphological (structural) features of the polymer systems. We therefore include a brief discussion about the role of structure on properties, highlighting issues of phase continuity and phase contrast. Finally, we discuss the advances made in polymer electrolytes for fuel cell applications and suggest directions for future generation materials.

VOLUME RELATED PARAMETERS

We move our discussion to focus on volume related parameters including: swelling ratio, water volume fraction, volume-based IEC (IEC_v), number of atom per charge (NAC), molar volume per charge (MVC) and percent conducting volume (PCV) - all presented in detail in the following sections. Hydration number (the number of water molecules per sulfonic acid site, often represented as λ), a non-mass based parameter although not strictly a volume related parameter, is also presented in terms of relevance for comparison purposes.

Swelling Ratio

The swelling ratio of a PEM is a widely reported volume related parameter but it is usually presented in the context of dimensional stability rather than in correlation with proton conductivity (44-51). Swelling ratio is obtained from thickness and/or length change(s) between hydrated and dry membranes:

$$\Delta T = \frac{(T - T_0)}{T_0}, \quad \Delta l = \frac{(l - l_0)}{l_0} \quad (2)$$

where T and T_0 are the thickness of membrane equilibrated in liquid water and in dry state, respectively, l and l_0 are the width or length of membrane equilibrated in liquid water and in dry state, respectively.

Swelling ratios allow for anisotropy to be investigated by measuring water uptake in the in-plane (x and y for extruded membranes) and through plane directions, while other length scale parameters only measure isotropic properties. Tang observed that Nafion

has a higher swelling ratio in the through-plane (z-) direction compared to the in-plane (x-, y-) directions at 30-90 % RH conditions (52). Others also reported anisotropic swelling ratios of sulfonated polyimides, polysulfones and Nafion (47, 53-55). The directionally oriented swelling ratio has importance because most conductivity measurements of sulfonated membranes are conducted in-plane while through-plane conductivity reflects in cell ohmic losses. A few reports have also indicated that Nafion has lower conductivity in the through plane-direction than the in-plane direction (56, 57).

Water Volume Fraction

Water volume fraction was introduced at least as early as 1980 (58). The volume water fraction, $WF_{(VOL)}$, of sulfonated polymer is calculated using the density of dry polymer and water, according to:

$$WF_{(VOL)} = \frac{(W_{WET} - W_{DRY}) \cdot \delta_{(dry)}}{W_{DRY} \cdot \delta_w} \quad (3)$$

where, W_{WET} and W_{DRY} are polymer weight in wet and dry states, respectively, $\delta_{(DRY)}$ and δ_w are the densities of the dry polymer and water, respectively.

In most cases, water volume fraction has been used to standardize proton conductivity (specific conductivity) in models. However, water volume fraction was also used for evaluation of different sulfonated polymers (59-62). Scherer et al. compared the proton conductivity of Nafion 117, Nafion 120 and Dow membranes using the number of carriers present per unit volume (63). Pintauro et al. compared proton conductivity of sulfonated poly phosphazene membranes using specific conductivity (64). Notes from

their observations are that i) the proton volume concentration of fully hydrated PFSA's did not always follow the same trends as mass based IEC, ii) dilution by water molecules affects proton conductivity and iii) Nafion and sulfonated poly phosphazene have similar dependence of proton conductivity on water volume fraction.

Hydration Number (λ)

Hydration number, the number of water molecules per sulfonic acid group (often denoted as λ), has been a widely used parameter to compare properties of sulfonated polymers. Since this parameter counts the number of water molecules per sulfonic acid group, it can be argued that it reflects length scales better than mass based parameters. This parameter has been used from the early 1960's for sulfonated styrene based ionomers (65). Since Bunce et al. reported water uptake of Nafion using λ , numerous papers used this parameter for quantifying water uptake of various sulfonated polymer system (26, 27, 66-68).

Hydration number has certain benefits as it reflects the "acid concentration" in water, assuming that all the water is in a hydrophilic phase and that all the acid groups also reside in this phase. The hydration level of sulfonated polymers under partially humidified conditions is a specific area that hydration number has been used. Zawodzinski et al. reported that Nafion has two isopiestic sorption regions: (i) relatively little increase of water content ($\lambda = 2-6$) with increasing humidity at low RH where the water in the polymer is engaged in strong interactions with the ionic components of the

polymer and (ii) a region of significantly greater increase of water content ($\lambda = 6-14$) where water is involved in polymer swelling at high RH (26, 27). Other sulfonated polymers show similar sorption behavior although the λ range in each sorption region varies. This observation motivated studies of the state of water in various sulfonated polymers and relationships between the state of water, proton conductivity, water diffusion and methanol permeability has been suggested (68-70).

For other areas such as electro-osmotic drag and water transport (27, 71-74), molecular dynamics modeling (75, 76), and analytical data analysis (77-80) of various sulfonated polymer systems, λ has been preferred over mass based water uptake for comparing polymer properties.

Although hydration number has been used as an alternative parameter for mass based water uptake or IEC (and in conjunction with them), it also has limits because it does not consider the relative abundance of water (hydrophilic vs. hydrophobic phase) in the membrane. Unlike swelling ratio and water volume fraction for which there is limited conductivity data available for multiple classes of polymer electrolytes under liquid equilibrated conditions, significant data for λ versus conductivity exists in the literature. Figure 2 shows proton conductivity of multiple sulfonated polymers as a function of λ . It is noted that the trend of increasing conductivity with increasing hydration number is still clear but the data scatter is slightly worse than conductivity versus IEC (Figure 1a).

[Fig. 2]

Volume Ion Exchange Capacity, IEC_V

Volume based ion exchange capacity (IEC_V) represents sulfonic acid concentration in a unit volume. IEC_V is obtained by multiplying the membrane density to weight based IEC (81, 82):

$$IEC_V = IEC \cdot \delta_{(DRY)} \quad (4)$$

where δ is density of dry membrane.

Considering volume expansion due to absorbed water, wet volume IEC, $IEC_{V(WET)}$ is obtained either by direct measurement or by estimating wet membrane density (81-83):

$$IEC_{V(WET)} = IEC \cdot \delta_{(WET)} = \frac{IEC_V}{(1 + WF_{(VOL)})} \quad (5)$$

where $\delta_{(WET)}$ is polymer density in the wet state and $WU_{(VOL)}$ is the volume water fraction.

In a previous report, we showed the strong importance of changing parameters from weight based IEC to $IEC_{V(WET)}$ in comparing polymers families. In these studies, comparing the water uptake and conductivity of hexafluoro bisphenol A (6F) and biphenol based sulfonated poly(arylene ether sulfone)s (BPSHs) showed a strong change in trends, as a function of IEC and $IEC_{V(WET)}$. The water uptake data (vol%) is reproduced in terms of both IEC and $IEC_{V(WET)}$ in Figure 3a and b, respectively. Of particular note, water uptake of the two polymer systems as a function of IEC showed the

exact same dependence on water uptake at a given IEC, which would lead to the conclusion that chemistry plays little role in water uptake. As the parameter changed from IEC to $IEC_{V(WET)}$, however, significant changes were witnessed that demonstrate the importance of chemistry on these systems.

[Fig. 3]

It is noted that both the fluorinated and non-fluorinated copolymers exhibit an inflection point (percolation threshold) as degree of sulfonation increases. The percolation threshold, water volume uptake for both 6F and BPSHs are similar (~ 60%). Further increase of degree of sulfonation reduced the $IEC_{V(WET)}$ where substantially increased water uptake resulted in reduced sulfonic acid group concentration (dilution of the acid groups). At this point mechanical properties of the system become a significant issue. From Figure 3b it is apparent that hexafluoro bisphenol A based copolymers have greater attainable maximum $IEC_{V(WET)}$ values than biphenyl copolymers. It is for this reason that they were able to attain higher conductivity values, as we reported earlier.

Figure 4 contains the data from Figure 3b, but also adds Nafion (at varying EW) and cross-linked sulfonated poly(arylene ether) (ESF-BP, at varying sulfonation level) (13). PFSA Nafion has greater attainable maximum $IEC_{V(WET)}$ than partially fluorinated polymers (6F), while cross-linked sulfonated poly(arylene ether)s (ESF-BPs) have even higher attainable maximum $IEC_{V(WET)}$. These results show clear trends that sulfonic acid

concentration per unit volume of hydrated polymers can be dramatically changed with fluorination and cross-linking.

[Fig. 4]

Figure 5 compares proton conductivity of BPSH copolymers as a function of (dry, weight based) IEC, and (hydrated, volume based) $IEC_{V(WET)}$. When the proton conductivity of BPSH is plotted as a function of IEC, conductivity increases monotonously until BPSH forms a hydrogel due to excessive water absorption. At this point, the polymer lacks the ability to resist swelling forces and eventually at even higher sulfonation levels results in dissolution. This behavior was also observed in other sulfonated polymer systems such as Nafion (12, 84), styrene sulfonic acids (85-87). If instead, the proton conductivity of BPSH is plotted as a function of $IEC_{V(WET)}$, much different trends appear. At low ion content, conductivity increases with increasing acid content, until some percolation limit is reached where mechanical properties become limited and swelling dramatically increases. Hydrogel formation also is denoted by the onset of decreased conductivity with further increasing of sulfonation level, even though the highly sulfonated BPSH polymers presented have reasonable conductivity, these hydrogels cannot be used for fuel cell applications because of poor mechanical properties that are more easily visualized in the plot containing $IEC_{V(WET)}$. In fact, even polymers above the percolation limit have poor long-term stability under fuel cell operating conditions.

[Fig. 5]

The data presented show the value of $IEC_{V(WET)}$ as a length scale parameter. Still, it has been rarely used (88), largely because of the lack of density data for sulfonated polymers in the literature due to the additional experimental requirements/difficulties of measuring volumetric change under fully and partially humidified (or dry) conditions.

It is worth noting, that Yeo et al. (89) and Makinnon et al. (90) have used similar quantities based on ion concentration within hydrophilic domains to make similar comparisons.

Number of Atom per Charge (NAC) and Molar Volume per Charge (MVC)

As most polymer systems presented in the literature have data based on mass based measurements and chemical structures, we have chosen to use this data to make estimates of volume based parameters using different levels of assumptions. A simple and rather rough estimation of sulfonic acid concentration can be expressed by number of atoms per charge (NAC), initially considering only the dry polymer. Table 1 shows the comparison of atomic mass, van der Waals and covalent radii of different atoms (91). While masses vary greatly, atomic radii are reasonably similar. For example, the atomic mass of fluorine is 19 times greater than that of hydrogen but the (van der Waals) atomic radius of fluorine is only 25% greater than that of hydrogen. Since the difference in atomic volume of each atom is much closer than their masses, the volume simply counting the number of atom per charge (92) should be an improved estimate compared to mass based comparisons. This dry NAC is analogous to mass based IEC or EW but it offers the

potential of more “fair” comparisons between fluorinated and non-fluorinated systems where the density differences are large.

[Table 1]

While, counting atoms represents an exceedingly simple mechanism to improve comparisons, it assumes each atom occupies the same volume and can be further improved on using group contributions of molar volumes to obtain a molar volume per charge (MVC) (93). While NAC approximates each atom has same volume, MVC accounts the van der Waals volumes increments of the composing atoms or structural groups.

$$MVC_{(WET)} = \sum_i n_i V_i \quad (6)$$

where V_i is the contribution of the i^{th} structural group which appears n_i times per charges.

MVC is an estimate of equivalent volume (cm^3 per ionomer/mole equivalent of acid groups) based on the summation of molar volume sub-units rather than true volume measurements. Table 2 shows examples of molar volume increments of selected groups used in our calculations (94, 95).

[Table 2]

Figure 6 shows proton conductivity of fully hydrated membranes as a function of (dry) NAC and MVC and can be compared with Figure 1b (which has larger data scatter) to support the use of volume based parameters compared to mass based parameters in predicting conductivity trends. Both plots show expected trends with conductivity increasing with decreasing volume per charge. Figure 6a (NAC) shows a slightly greater data scatter than Figure 6b (MVC) as might be expected due to the increased level of sophistication in obtaining MVC. Still, NAC shows reasonably clear trends and suggests that counting the number of atom per charge may be a useful metric in comparing conductivity between polymers.

[Fig. 6]

Fully hydrated versions of these properties, $NAC_{(WET)}$ and $MVC_{(WET)}$, can be calculated from the dry based properties and information on water uptake:

$$NAC_{(WET)} = NAC + 3\lambda \quad (7)$$

$$MVC_{(WET)} = MVC + 18\lambda \quad (8)$$

where λ is the hydration number, 3 is the number of atom in a water molecule and 18 is molar volume of water in cm^3/mol .

Figure 7 shows proton conductivity of BPSH and other sulfonated polymers as a function of $MVC_{(WET)}$ ($NAC_{(WET)}$ shows similar trends and was therefore excluded). As degree of sulfonation of BPSH increased from 20 to 35%, $MVC_{(WET)}$ decreased then increased with further increased of degree of sulfonation. This behavior mirrors that of Figure 5b for $IEC_{V(WET)}$, and reflects the percolation threshold and hydrogel formation that appear at 35 and 45% sulfonation, respectively. This suggests that $MVC_{(WET)}$ (and/or $NAC_{(WET)}$), which can be calculated from data commonly reported in the literature can be considered as an alternative to $IEC_{V(WET)}$, which is more difficult to obtain experimentally and often not reported in the literature. This is not surprising as $MVC_{(WET)}$ is an estimate of equivalent volume, and equivalent volume is the inverse of $IEC_{V(WET)}$. While trends within a polymer family are discernable, the scatter of conductivity data as a function of $MVC_{(WET)}$ (or $NAC_{(WET)}$, and therefore likely $IEC_{V(WET)}$) is high leaving these parameters as poor predictors of conductivity.

[Fig. 7]

Percent Conducting Volume (PCV)

$IEC_{V(WET)}$, $NAC_{(WET)}$, $MVC_{(WET)}$ correlate poorly with proton conductivity, perhaps because water is only considered as a volume element for concentration purposes rather than being the phase through which conduction occurs. We also present an alternative parameter, percent conducting volume (PCV) that focuses on the conducting (hydrophilic) domain (93).

We define percent conducting volume (PCV) as

$$PCV = \frac{V_{H_2O} \cdot \lambda}{MVC_{(WET)}} \quad (9)$$

where V_{H_2O} is the molar volume of water, 18 cm³/mol.

The numerator of equation 9 is an estimate of the volume of the aqueous (hydrophilic) phase per acid site, and the denominator is an estimate of the volume of the hydrated membrane (both hydrophilic and hydrophobic phases) per acid site. PCV is essentially a ratio of the volume of the hydrophilic phase to the hydrated membrane analogous to the conducting volume of the membrane (which could be measured experimentally, but is rarely reported).

Figure 8 shows proton conductivity of multiple sulfonated polymers under fully humidified conditions as a function of PCV. A stronger correlation between proton conductivity and PCV is seen compared to any of the other approaches discussed, and PCV seems to be a reasonable predictor for proton conductivity. Proton conductivity increases significantly with PCV from 0.1 to 0.4 and then only marginally above 0.4. These results suggest targeting PCV values ~0.3-0.4 where conductivity is high, but mechanical properties can be retained due to higher hydrophobic domain content. In fact, many “optimized” polymer systems fall in this range.

[Fig.8]

It is also noted that PFSA and sulfonated polyaromatics have similar proton conductivity at a given PCV under fully humidified conditions, in stark contrast to the significantly higher conductivity reported for PFSA compared to sulfonated polyaromatics when compared using mass normalized ion content. This plot suggests that the conductivity difference of PFSA and sulfonated polyaromatics under fully humidified conditions is rather negligible when compared using a volume based metric. Furthermore, we did not observe any clear, systematic differences of conductivity depending on acidity of acid group, micro-phase separation, hydrophobicity, chain rigidity, distribution of sulfonic acid groups and/or various polymer architectures. Multi-block copolymers, random copolymers, graft copolymers and crosslinked systems all exhibited very similar conductivity at a given PCV. This suggests, somewhat surprisingly, that structural or morphological effects have little effect on proton conductivity under fully humidified conditions.

Table 3 summarizes the features of various parameters presented in terms of ease of acquisition, factors accounted for, and correlation with proton conductivity for liquid equilibrated polymer membranes. While mass based parameters are the most commonly reported, they have significant limitations in their applicability as previously discussed, while non-mass based measurements offer advantages when making specific comparisons. Swelling ratio, water volume fraction and hydration number take into account the volume content of water absorbed in sulfonated polymers. IEC_v , NAC and MVC parameters express sulfonic acid concentration in dry and wet conditions, with the

wet volume based parameters providing useful information on percolation and hydrogel formation of sulfonated polymers. PCV showed the strongest correlation with proton conductivity and was obtained through information available in the literature for many different families of polymers. While each of these parameters has utility they also all have limitations, and the data even with PCV shows significant scatter and the cases thus far presented only represent liquid equilibrated membranes.

[Table 3]

Under partially hydrated conditions the data scatter of proton conductivity increases substantially versus PCV, as shown in Figure 9 (23, 35, 96-106). PCV of sulfonated polymers change as λ decreases with reduced RH along with a corresponding change in conductivity. The data in Figure 9 is limited to the cases in the literature where conductivity is reported as a function of λ .

[Fig.9]

A likely explanation for the greater data scattering in Figure 9 compared to Figure 8 is the morphological differences of polymer systems under full and partial humidification. Most sulfonated polymers are visualized as having phase separated structure due hydrophobic (non-sulfonated) and hydrophilic (sulfonated) polymer segments. Since proton conduction occurs in hydrophilic domains, morphological difference should affect

conductivity both in fully hydrated and partially hydrated conditions. However, a greater impact is observed under low humidification. As polymers dehydrate, the number of water molecules per sulfonic acid group decreases; affecting the hydrophilic domain size, and likely, in many cases, the continuity of the proton conducting pathways. The data presented in Figure 8 suggests these factors are not particularly important under full humidification, but the data in Figure 9 suggest under partial humidification they can play a large role. We attribute these differences in behavior to specific morphological factors.

MORPHOLOGICAL EFFECTS

Morphological effects can include many aspects of polymer structure such as ion aggregation, domain size, domain connectivity, size of water channel, and others (107-114). Although structural information is difficult to quantify, we choose to promote phase contrast and phase continuity as qualitative aids in interpreting the impact of structural effects on observed properties. Figure 10 illustrates two dimensional renderings of these two parameters (phase contrast and continuity) in schematic diagrams of phase separated polymers. Filled circle represents hydrophilic polymer segment (or water) and empty circle represents hydrophobic segment. Phase contrast is meant to define the extent of phase separation between the hydrophilic and hydrophobic domain (not necessarily the difference between hydrophilicity and hydrophobicity of polymer domains themselves, although increased differences in hydrophobicity would be expected to lead to increased phase contrast). Polymer having lower phase contrast (Figure 10a) have less defined phase separation than those having higher phase contrast (Fig. 10b).

PFSAs such as Nafion exhibit highly phase contrasted structures, presumably due to the extreme hydrophobicity and flexibility of the perfluorinated ethylene backbone combined with the mobility and hydrophilicity of the sulfonic acid containing side chain. The large driving force for phase separation in these polymers is evidenced by solubility parameter. PFSAs have large differences in solubility parameters for hydrophobic and hydrophilic segments compared to non-fluorinated polymers (e.g. $16 \text{ J}^{1/2}\text{cm}^{-3/2}$ for Nafion versus $9 \text{ J}^{1/2}\text{cm}^{-3/2}$ for sulfonated poly ether ketone) (115, 116). The highly phase contrast impacts structure and thereby affects observed properties as has been reported elsewhere in significant depth. (68, 108, 117-119).

Phase continuity is meant to reflect the connectedness of ion conducting (hydrophilic) domains, and is also illustrated in comparisons of Figure 10. While Figure 10c shows relatively poor phase contrast, it shows enhanced phase continuity compared to Figures 10a and b. Phase continuity is necessary to provide the pathways for proton conduction.

[Fig. 10]

Phase continuity can be probed by microscopy and has been reported upon for multi-block and graft copolymer architecture (112, 120-122). Figure 11 shows the tapping mode – atomic force microscopy micrographs (TM-AFM) of 5 different sulfonated polymers which have similar MVC at 50% RH: **a**: non-fluorinated random copolymer (BPSH-35), **b**: partially fluorinated random copolymer (6F-40), **c**: perfluorinated random copolymer (Nafion 212), **d**: non-fluorinated alternating polymer (Ph-PEEKDK), **e**: non-

fluorinated random copolymer (same as **a**, reproduced to aid visual interpretation) and **f**: non-fluorinated multi-block copolymer (BPSH-PI 15k-15k). It is expected that phase contrast increases from **a** to **b** and from **b** to **c** due to increased backbone fluorination and backbone flexibility (although this is not apparent in Figure 11 because of the arbitrary nature of the color scale used. In general, all three AFM show qualitatively similar domain size and phase continuity). Samples **d**, **e** and **f** show clear trends with increasing phase continuity from **d** to **e** and from **e** to **f** due to differences in copolymer architecture. The multi-block copolymer, **f**, has excellent phase continuity while the alternating homopolymer, **d**, showed basically featureless phase structure absent of clear micro phase separation.

[Fig.11]

We use the generalities placed forward in our discussion of Figure 11 to evaluate the proton conductivity of these sulfonated copolymers under partially hydrated conditions, plotted as a function of PCV in Figure 12. Figure 12 clearly shows clear trends as proton conductivity increased with fluorination. For example, proton conductivity of perfluorinated Nafion is greater than the partially fluorinated 6F-40 which in turn has a higher conductivity than the non-fluorinated BPSH-35 across the range of PCV values reported. More than an order of magnitude conductivity difference exists at some PCV values, and it is our suggestion that phase contrast is playing a critical role at low RH. We also examined the proton conductivity of other PFSA membranes including short side chain PFSAs and different EW Nafion, which shows very similar conductivity at a given

PCV (plot was omitted for brevity). Figure 12 also shows the trend that the proton conductivity of multi-block copolymer is greater than random copolymer and alternating homopolymer indicating that better phase continuity is another critical parameter for low RH conductivity. The trends for phase continuity across polymer families are consistent with other studies within a polymer family as a function of increasing sulfonation level (123-125)

[Fig. 12]

DESIGN PERSPECTIVE OF SULFONATED POLYMERS FOR FUEL CELLS

From our studies of the wide range of polymers presented in the literature, we have found that under fully humidified conditions, proton conductivity is predominantly influenced by factors that can be expressed by a single parameter, PCV. These findings suggest that at high hydration levels, factors such as morphology, acidity, and backbone hydrophobicity have negligible impact on proton conductivity.

At lower levels of hydration, where membranes are being developed for high temperature, low RH application, factors such as phase continuity and phase contrast have been presented as properties that can be exploited for improved conduction. Increased levels of fluorination and the use of multi-block copolymer architectures were two routes presented that resulted in increased conductivity at given PCV values.

From the analysis presented it can be suggested that sulfonated polymers require highly localized (maximizing phase contrast), highly continuous hydrophilic phase domains, and highly concentrated sulfonic acid concentration for low RH fuel cell operations. This mirrors the direction of much of the research community where there is a push for increased acid content within the conducting phase and more clear separation from the structural phase. As many of these materials are intended for transportation applications where there is the need for starting under cold, wet conditions and operation under hot, dry conditions, issues relating to RH and temperature cycling are also critical, and to date, the rubbery nature of PFSA ionomers have led to enhanced durability compared to hydrocarbon and wholly aromatic polymers.

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Table 1. Atomic mass, van der Waals radius and covalent radius of different atoms

[Pauling]

	-H	C _{ar}	-N<	-O-	-F	-S-
Atomic mass	1.008	12.01	14.01	16.00	19.00	32.07
Van der Waals Radius (nm)	0.120	0.170	0.157	0.136	0.135	0.185
Covalent Radius (nm)	0.031	0.070	0.070	0.066	0.064	0.104

Table 2. Molar volume increments of amorphous polymer [Van Krevelen, Properties of Polymers]

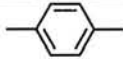
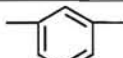
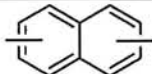
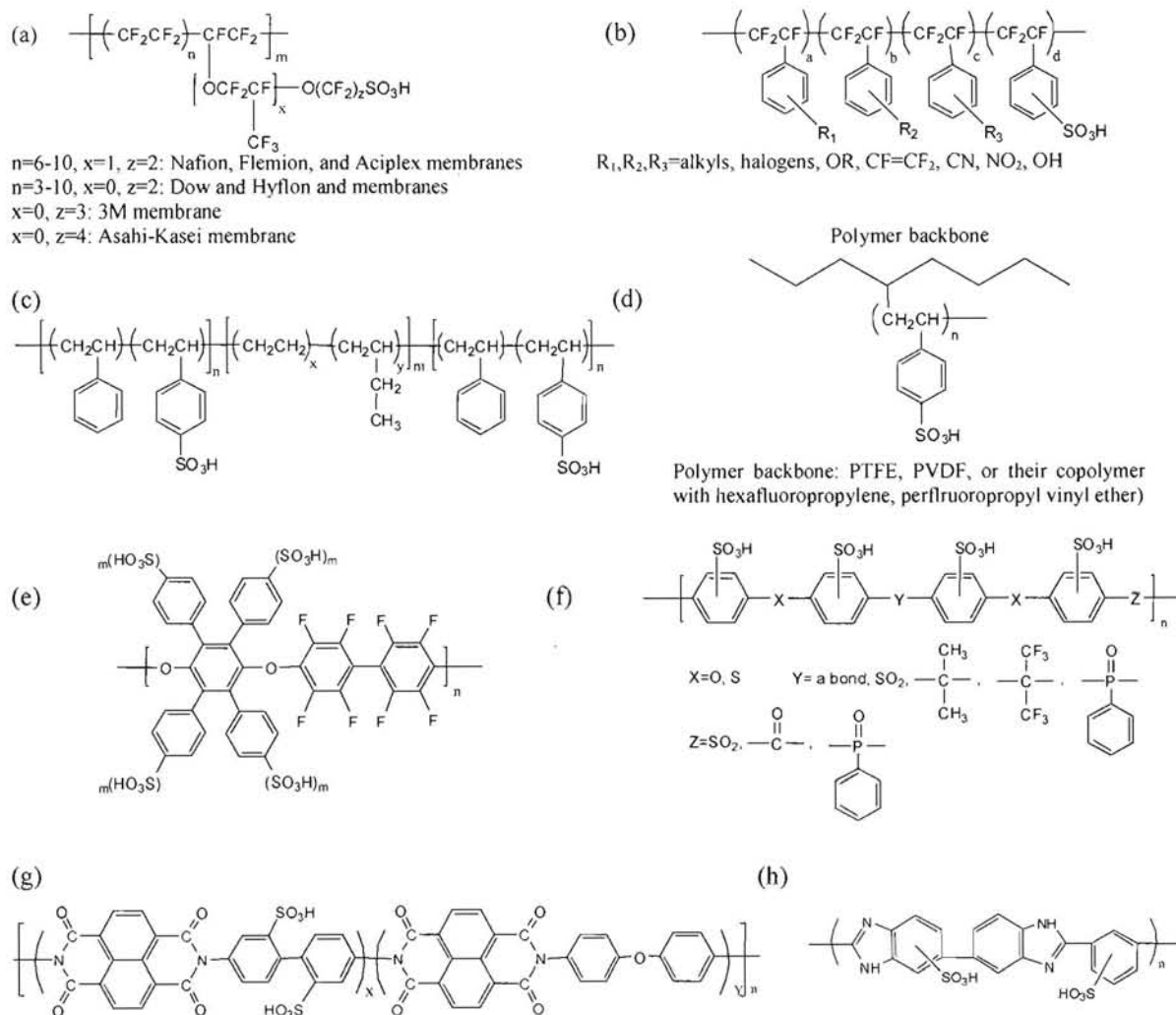
Groups	V_a (298) (cm^3/mol)	Groups	V_a (298) (cm^3/mol)
$\text{—}\overset{\text{H}_2}{\underset{\text{—}}{\text{C}}}\text{—}$	16.37	$\text{—}\overset{\text{O}}{\underset{\text{O}}{\parallel}}{\text{S}}\text{—}$	32.5
$\text{—}\overset{\text{F}_2}{\underset{\text{—}}{\text{C}}}\text{—}$	23.7		
$\text{—CH(C}_6\text{H}_5)\text{—}$	84.16		65.5
—CH(CN)—	30.7		
—CHF—	20.0		69
$\text{—C(CH}_3)_2\text{—}$	49.0		
$\text{—C(CH}_3)(\text{C}_6\text{H}_5)\text{—}$	100.5		112
$\text{—}\overset{\text{H}}{\underset{\text{—}}{\text{N}}}\text{—}$	17.3		
—O— (al.)	8.5	$\text{—}\overset{\text{—}}{\underset{\text{—}}{\text{C}}}\text{—}$	5.28
—O— (ar.)	8.0		
$\text{N}_{\text{ar}} (\text{pyrid})$	8.32	$\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$	18.72
$\text{—SO}_3\text{H}$	40.5	—CF_3	34.08

Table 3. Comparison of mass and length scale parameters.

Parameter		Ease	Factors accounted for*		Correlation with conductivity
			Water content	Sulfonic acid concentration	
Mass based	Water uptake	Easy	Yes	No	Medium
	Ion Exchange Capacity (IEC)	Easy	No	Yes (dry state)	Poor
Non-Mass based	Swelling ratio	Easy	Yes	No	NA
	Water volume fraction, ($WF_{(VOL)}$)	Medium	Yes	No	NA
	Hydration number, (λ)	Easy	Yes	No	Poor
	Volume Ion Exchange Capacity, (IEC_V)	Difficult	No	Yes (dry/wet state)	NA
	Number of Atom per Charge, (NAC)	Easy	No	Yes (dry/wet state)	Medium
	Molar Volume per Charge, (MVC)	Easy	No	Yes (dry/wet state)	Medium
	Percent Conducting Volume, (PCV)	Easy	Yes	Yes (wet state)	Good

* All parameters do not account morphological features



Scheme 1. Chemical Structure of various sulfonated polymers (a) PFSA, (b) sulfonated polystyrenes, (c) sulfonated polystyrene-*b*-(ethylene-*co*-butylene)-*b*-sulfonated polystyrenes, (d) radiation-induced polystyrene graft polymers, (e) sulfonated polyphenylenes, (f) sulfonated aromatics, (g) sulfonated polyimide, and (h) sulfonated polyimidazoles

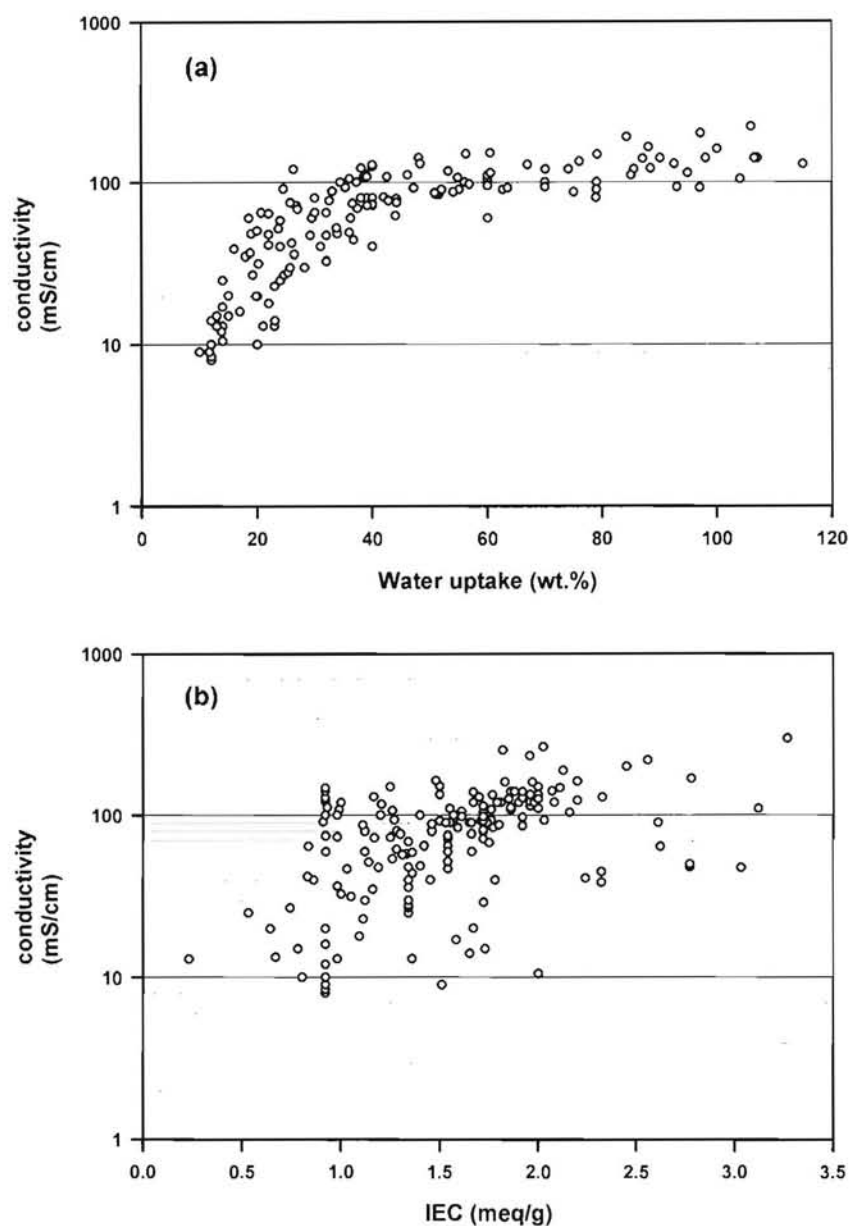


Fig. 1. Proton conductivity as a function of (a) water uptake and (b) weight based IEC (IEC) of multiple sulfonated polymers; Proton conductivity under fully hydrated conditions at ambient temperature was taken from the literature (10-41)

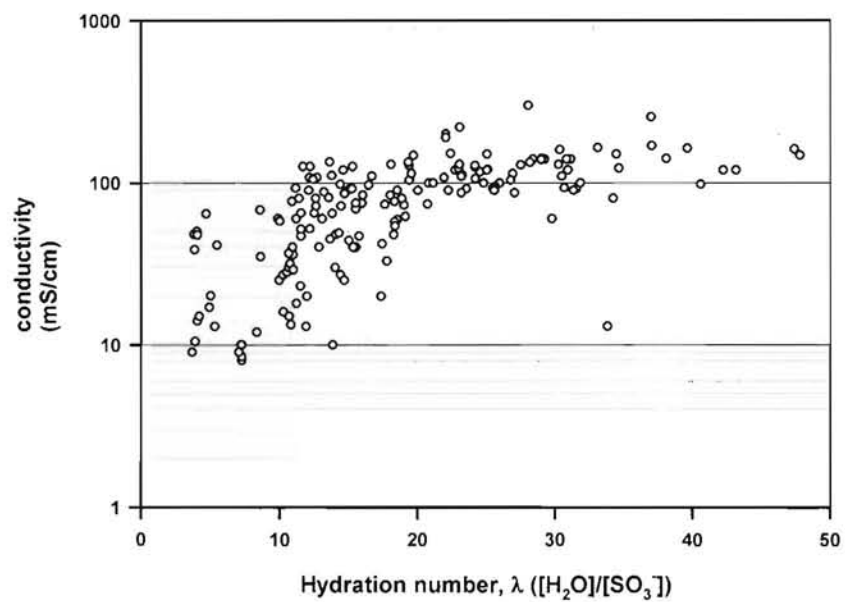


Fig. 2. Proton conductivity as a function of hydration number of multiple sulfonated polymers under fully hydrated conditions at ambient temperature.

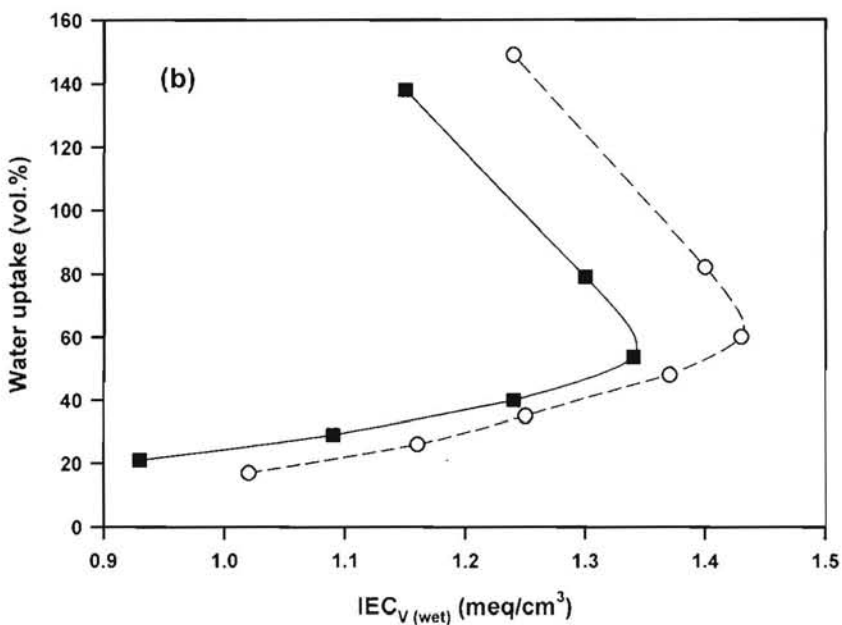
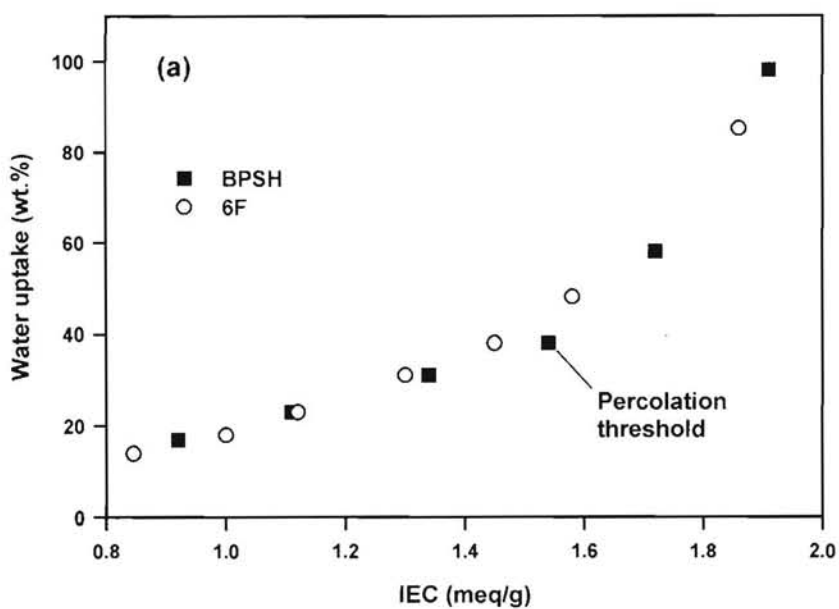


Fig. 3. Comparison of water uptake using (a) weight based IEC and (b) fully hydrated, volume based IEC ($IEC_{V(WET)}$). Data reproduced from ref. (81).

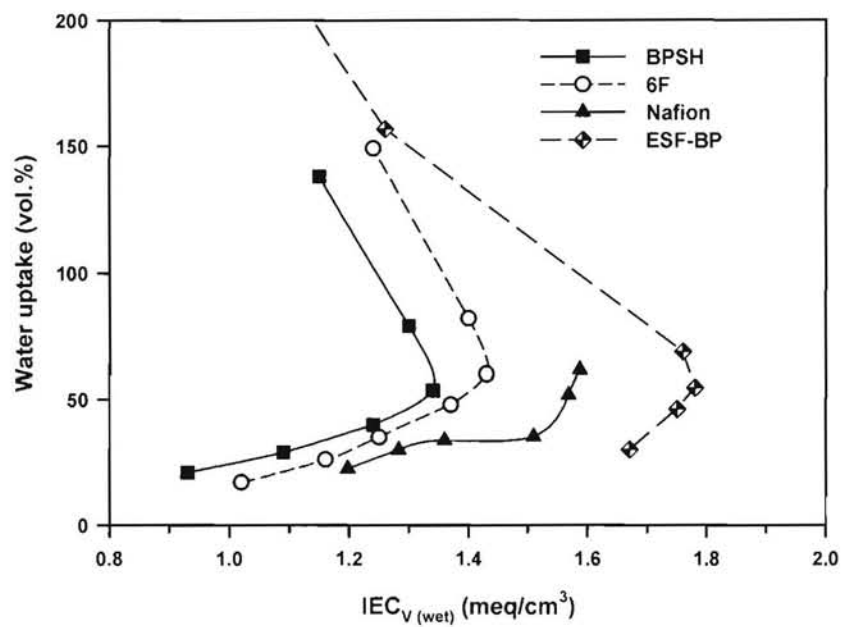


Fig. 4. Effect of fluorine and cross-linking on membrane water uptake as a function of $IEC_{V(wet)}$.

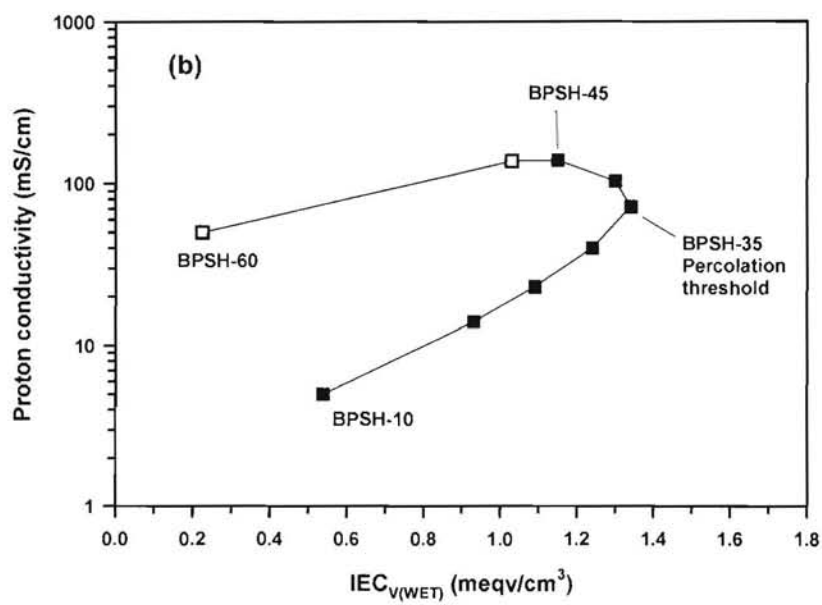
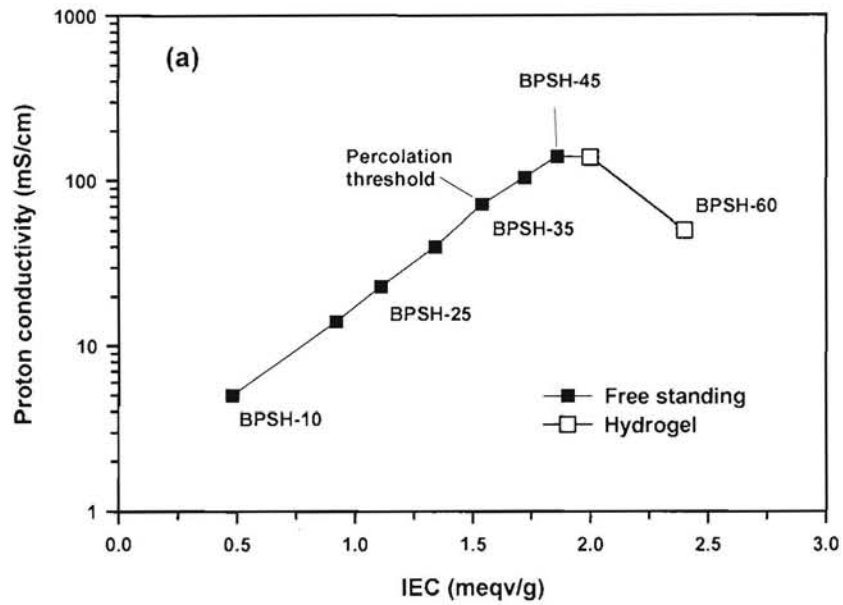


Fig. 5. Comparison of proton conductivity using (a) weight based IEC and (b) fully hydrated, volume based IEC ($IEC_{V(WET)}$).

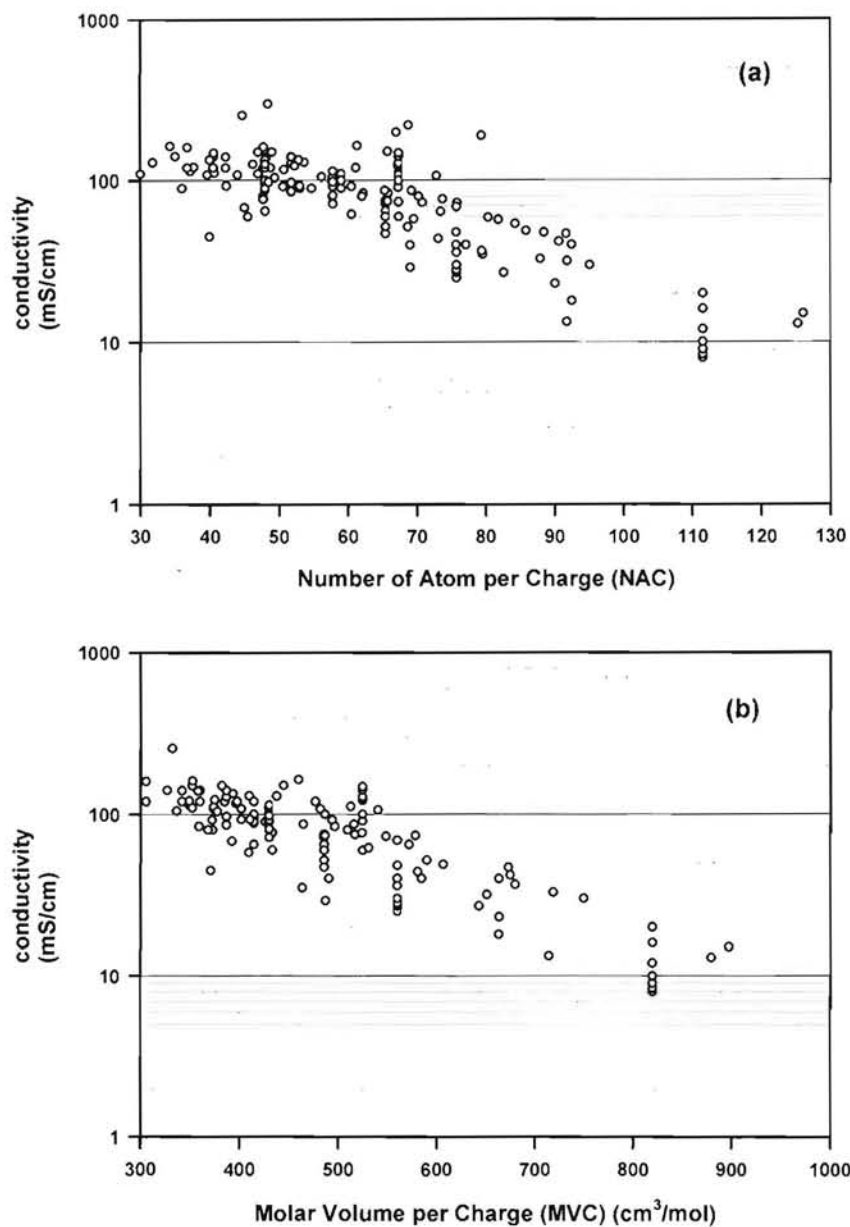


Fig. 6. Proton conductivity versus dry (a) NAC and (b) MVC of various sulfonated polymers under fully hydrated conditions at ambient temperature.

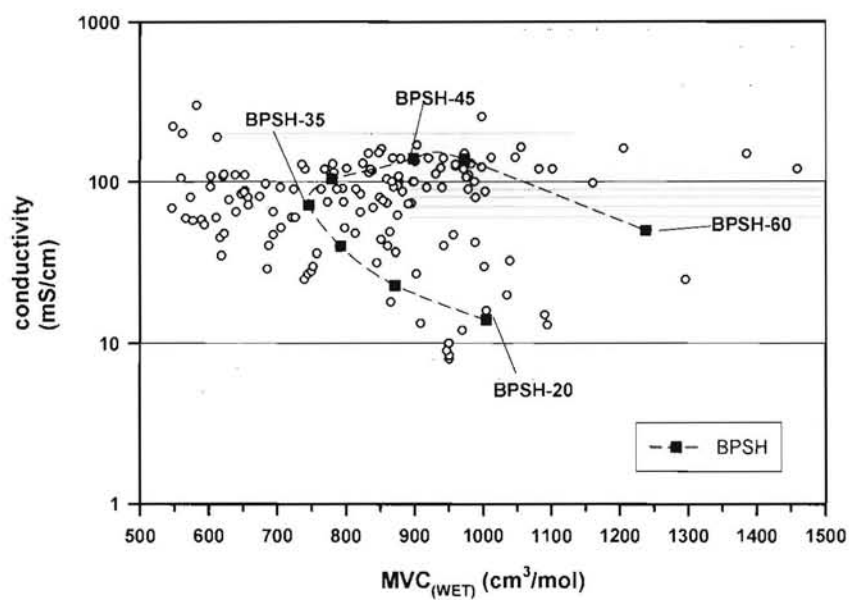


Fig. 7. Proton conductivity versus (a) $MVC_{(WET)}$ for sulfonated polymers (BPSH polymers highlighted) under fully hydrated conditions at ambient temperature.

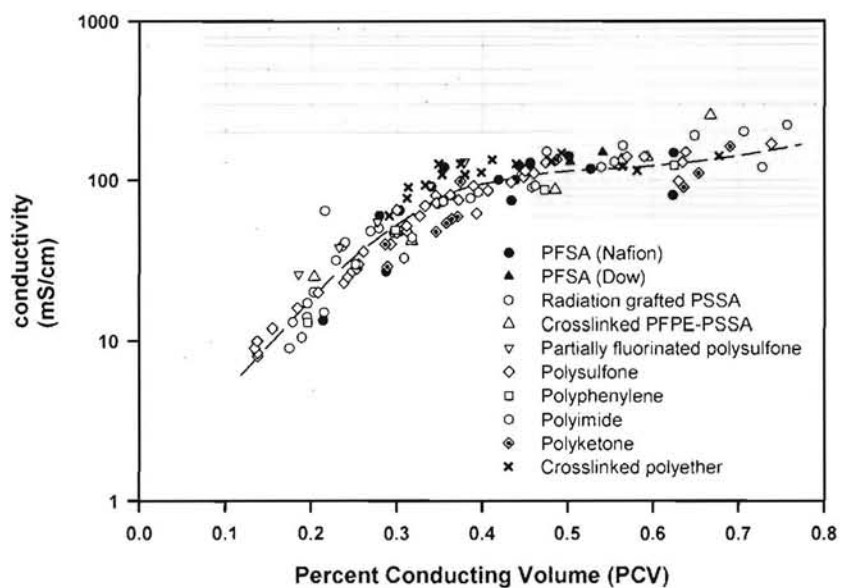


Fig. 8. Proton conductivity versus percent conducting volume of various sulfonated polymers under fully hydrated conditions at ambient temperature.

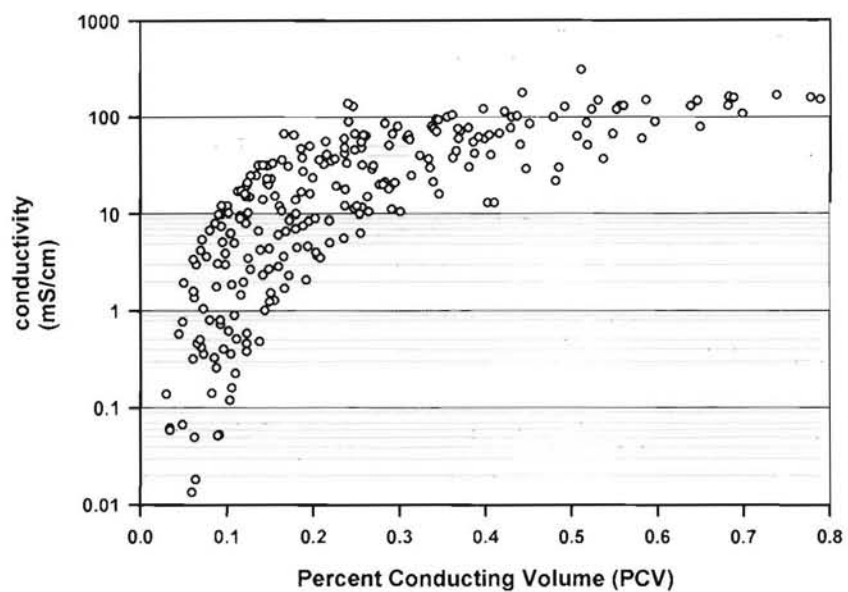


Fig. 9. Proton conductivity versus percent conducting volume of various sulfonated polymers under partially hydrated conditions at ambient temperature as taken from the literature (23, 35, 96-106)

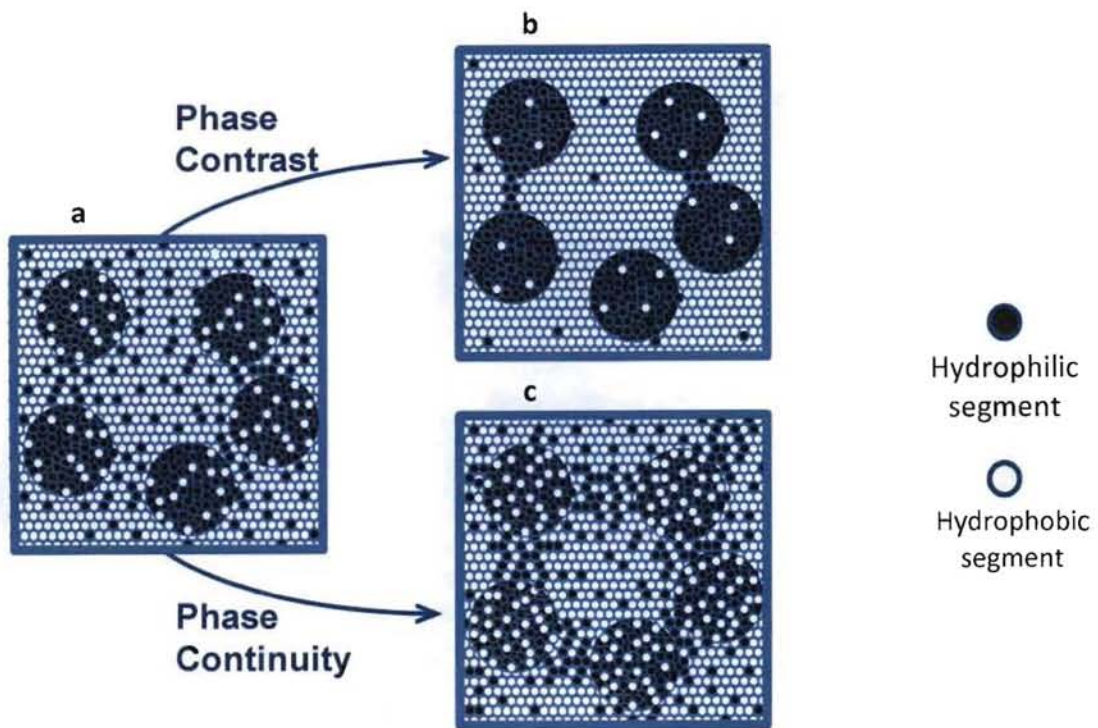


Fig. 10. Schematic representations of phase contrast and phase continuity

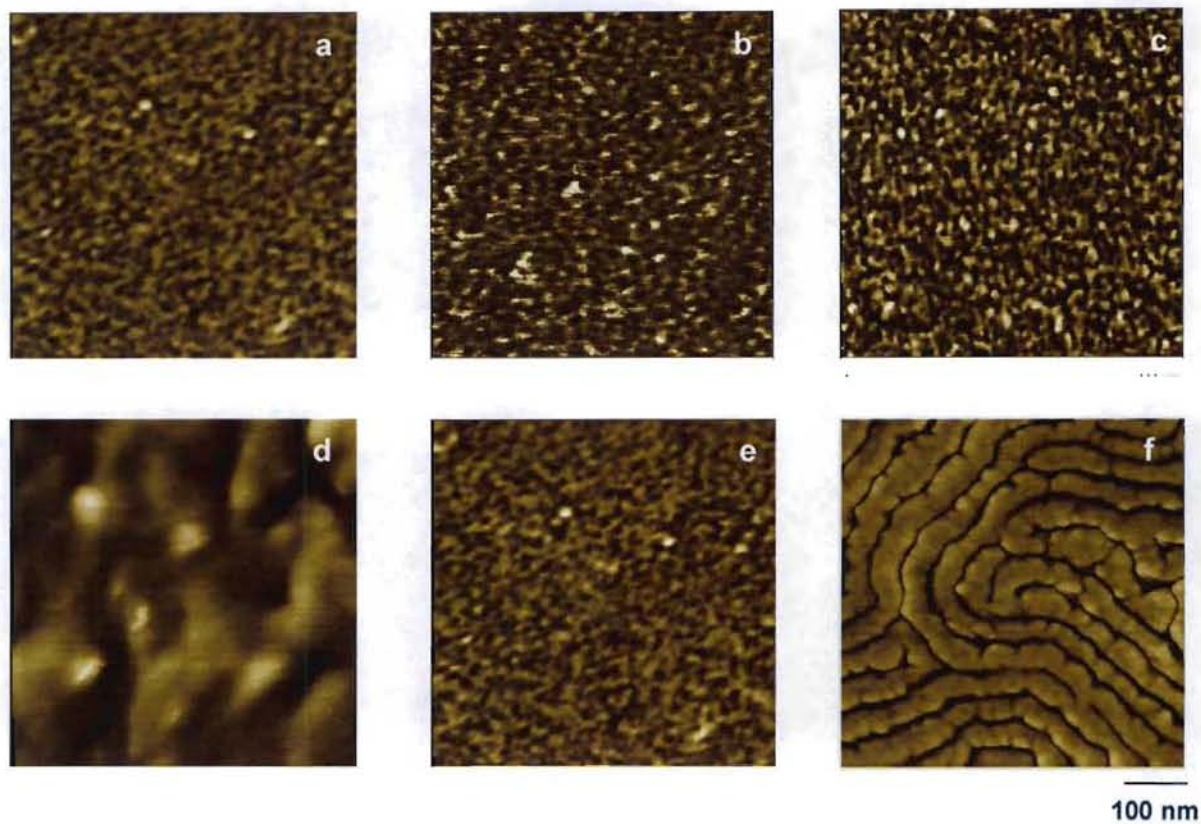


Fig. 11. Tapping mode AFM images of **a**: non-fluorinated random copolymer (BPSH-35), **b**: partially fluorinated random copolymer (6F-40), **c**: perfluorinated random copolymer (Nafion 212), **d**: non-fluorinated alternating polymer (Ph-PEEKDK), **e**: non-fluorinated random copolymer (BPSH-35) and **f**: non-fluorinated multi-block copolymer (BPSH-PI 15k-15k).

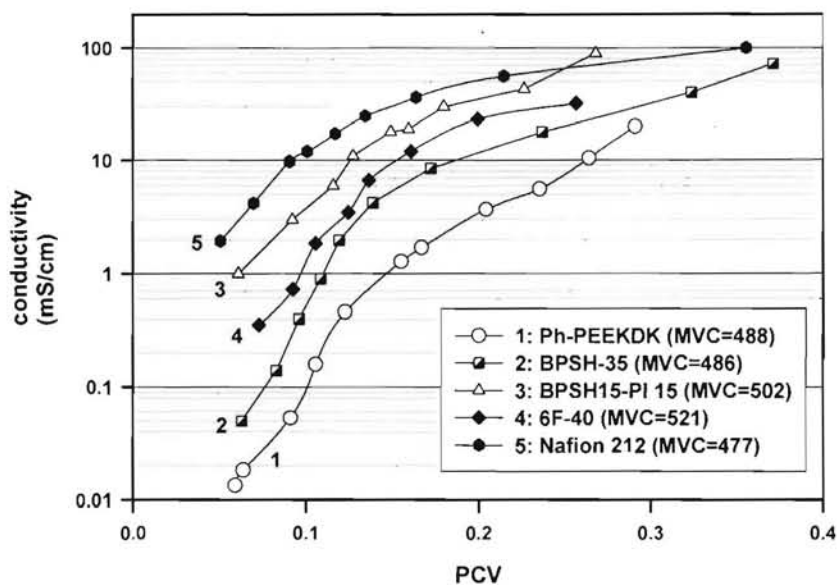


Fig. 12. Proton conductivity vs. PCV of non-fluorinated alternating polymer (Ph-PEEKDK), partially fluorinated random copolymer (6F-40), perfluorinated random copolymer (Nafion 212), non-fluorinated random copolymer and non-fluorinated multi-block copolymer: PCV changes with RH.